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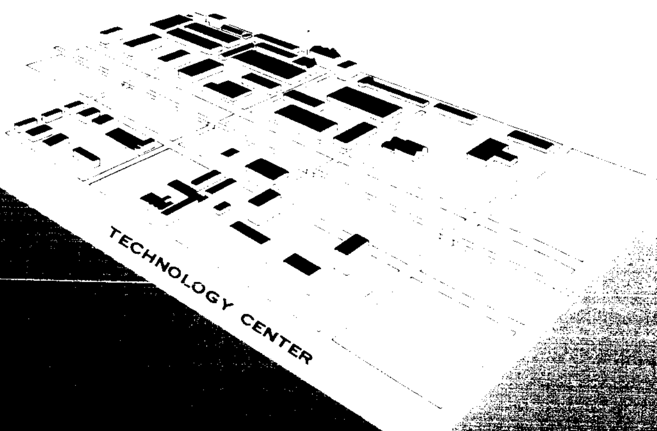

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ARF 1220 - QR 3

(Quarterly Technical Report No. 3)

INVESTIGATION RELATING TO THE DEVELOPMENT OF CADMIUM TELLURIDE ENERGY CONVERTERS

National Aeronautics and Space Administration
Headquarters

ARF 1220 - QR 3
(Quarterly Technical Report No. 3)

INVESTIGATION RELATING TO THE DEVELOPMENT OF CADMIUM TELLURIDE ENERGY CONVERTERS

(Covering the Period from 11 January, 1963 to 10 May, 1963)

Contract No. NASw - 455
ARF 1220 - QR 3

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FOREWORD

This is the third Quarterly Report on an Investigation Relating to the Development of Cadmium Telluride Energy Converters for the National Aeronautics and Space Administration under Contract No. NASw-455, covering the period January 11, to April 30, 1963.

During this period, while the effort has been centered mainly on development and exploitation of the vertical refining technique, a number of annoying and delaying practical problems has prevented really satisfactory operation of the method. Personnel who have contributed to this report are R. J. Robinson, M. Scott and A. P. van den Heuvel. Data are recorded in ARF logbooks 12753, 12754 and 12755.

Respectfully submitted,

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ABSTRACT

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Development of the vertical zone refining process has continued during this quarter. However, several small problems have arisen, and less progress was made in this direction than was anticipated in the previous report. These delays have taken the form of zone heater failure, intermittent sticking of the cadmium telluride to the quartz tube and devitrification of the quartz tube in the presence of platinum. The solution to these problems is expected to be provided by a new furnace specifically made for this new technique. Despite the set backs, we still feel confident of the ultimate success of the technique, especially since discovering that a similar approach has been used with success on alloys of bismuth telluride by researchers at General Electric. In our future work we plan to develop the vertical process to a reliable stage and to optimize those parameters which will ultimately determine the performance of CdTe as a solar energy converters.

Author

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INVESTIGATION RELATING TO THE DEVELOPMENT OF CADMIUM TELLURIDE ENERGY CONVERTERS

I. INTRODUCTION

This is the third Quarterly Report on an Investigation Relating to the Development of Cadmium Telluride Energy Converters for the National Aeronautics and Space Administration under Contract Number NASw-455, covering the period January 11, to April 30, 1963 inclusive. The nature of the programme is to investigate the feasibility of utilizing cadmium Telluride (CdTe) as a photovoltaic solar energy converter. The objectives of this contract are the construction of experimental cadmium telluride single crystal solar cells and the measurement of their electrical properties.

As indicated in the previous report under the heading "Future Work", emphasis has continued to be put on the material preparation end of the study in view of its ultimate control of the performance of any device fabricated from the material.

It was anticipated, from the encouraging results obtained in the previous quarter, that most of the snags involved with the new approach would be easily overcome and that a regular system for producing single crystals would be quickly established. Unfortunately, this has not proved to be the case. The delays have not been due so much to any disadvantages inherent in the method. Practical difficulties have appeared associated with running small heating coils at the high temperatures necessary to zone refine CdTe, preventing sticking and tube fracture, establishing uniform temperature zones, and automating the present apparatus so that overnight runs can be performed.

However most of these problems will be solved in the near future when the new apparatus, specifically designed for vertical operation, becomes available. It is at present going through the machine shop.

Physical and electrical measurements on those boules which have been produced or removed from fractured tubes have been somewhat inconclusive. Success so far has been limited to a maximum of two passes before the zone heater broke down and under these conditions it is hardly surprising that single crystals have not been obtained, since the first pass is usually carried out on the powdered material to form it into a solid mass. Electrical measurements on the multi-crystalline material have shown it to be of relatively low resistivity and n-type.

The last section of this report indicates the direction planned for future work.

II. VERTICAL ZONE REFINING AND CRYSTAL GROWTH

a). The Problems Encountered and Their Solution

As described in the previous quarterly report the new approach is to zone refine the CdTe initially in sealed quartz tubes. On the first two occasions when this technique was attempted no sticking was encountered and the results were therefore reported as encouraging. However, subsequently, it was found that sticking did still occur on occasion resulting in fractured tubes and ruined heater coils. This problem has now been completely solved by introducing a small quantity of hydrogen into the tube prior to sealing off from the vacuum system. This method is in accord with the observation reported by Lawson and Nielson[1] that cadmium metal evaporated in vacuum adheres strongly to a clean quartz surface but does not do so if the operation is carried out in the presence of hydrogen gas. The alternative approach of using a pyrolitically deposited carbon film is possible but is less preferable from the purity viewpoint as well as being a possible source of numerous nucleation sites.

Another problem which has been a continuing source of delay has been the physical breakdown of the zone heater itself. When this occurs it also often results in a fractured tube due to the sudden local cooling which results. In principal the problem is trivial. The breakdown occurs when nichrome heating elements are employed and is partly due to both the high electrical loading on the coil, and the low strength of nichrome at elevated temperatures, but is mainly the result of running the heater near its maximum permissible temperature. The obvious solution, where an oxidizing atmosphere is involved is to use platinum, which has a melting point above $1500^{\circ}C$, well above the m.p. of CdTe. Unfortunately, however, platinum heaters are incompatible with quartz tubes at high temperatures due to a devitrification of the quartz which takes place under these conditions. Indeed, even the Pt-Pt (10% Rh) thermo-couple used to monitor the zone temperatures tends to cause some devitrification of the tubes. Attempts to protect and support the nichrome heaters from the atmosphere by coating them initially with Sauereisen refractory cement No. 6 has proved only partly successful as has a similar procedure on the Pt heaters to protect the quartz tubes. In both cases so far it has merely resulted in slightly extended lifetimes, but still not long enough for sustained operation over several zone passes.

All these problems are expected to be solved when the new furnace, which has been specifically designed for vertical zone refining of CdTe, is completed. The furnace at present in use was a quick mock-up to establish the practicability and effectiveness of the approach. The new furnace, modeled after the first one, will have a non-porous alumina tube as the furnace tube and will have demountable water cooled seals at each end. By this means refractory materials such as tungsten, molydenum, tantalum or carbon may be employed to form the zone heater, resulting in a much greater lifetime for this part of the equipment, in addition to enabling still higher temperatures to be employed if this is found to be desirable.

In addition the new furnace will be able to operate completely automatically so that zone refining experiments can be continued overnight and not be restricted to periods when an operator can be present. This should speed up this end of the project considerably.

b) Discussion

While apparent progress in the form of actually producing high quality single crystal boules has undeniably been slow, due to the initial difficulties in developing a new technique, we still firmly believe in both the essential correctness of this approach and in its ultimate success. Support for this view, quite apart from the initial success reported in the previous Quarterly report, is provided by the experiments of F. K. Heumann at the General Electric Research Laboratory on alloys of bismuth telluride. In a paper published in the April, 1962 edition of the Journal of the Electrochemical Society, he reports considerable success in zone refining, zone leveling and single crystal growing of these alloys by a vertical technique essentially identical to that arrived at independently in this laboratory. In the paper, the point is made that the technique is particularly suitable for zone melting decomposable compounds or compounds with high vapor pressure constituents, as is the case for CdTe. Unfortunately, the zone temperatures employed in Heumann's experiments were around 550°-600°C and so did not involve the problems which we have encountered and have had to solve.

III. ELECTRICAL MEASUREMENTS

A continuing attempt has been made to monitor the electrical properties of that material which has been produced so far. As mentioned previously however, this has so far invariably been somewhat polycrystalline though dense material. It has been made up of quite large (several millimeters across) single crystals, compared to the boules produced in the horizontal zone refining experiments. In view of all the foregoing facts, the electrical measurements are not too meaningful from a device viewpoint since a really successful zoning has not been achieved. Resistivity profiles on slices cut from sample boules show several barriers within a single slice, while the resistivity between barriers varies from a few ohm-cm to around 100 ohm-cm. Those Hall measurements made so far show the material to be n-type, suggesting excess cadmium atoms acting as donors. This characteristic of the vertical technique to produce n-type material is duplicated by methods using the Bridgeman technique, although there is an apparent anomaly in that results obtained here suggest that the cause is due to the absence of a cadmium back pressure. (It is to be recalled that in the horizontal zone refining experiments where cadmium back pressure was employed to prevent sublimation the material turned out to be p-type suggesting cadmium vacancies being present as acceptors).

It would seem that the explanation of this apparently contradictory behavior is as follows. In the horizontal zone refining experiments, although there is excess cadmium in the melted zone (which is the cause of the bubbling and consequent porosity), after solidification the material is free to come to equilibrium with the prevailing cadmium vapour pressure. This is usually less than that required to maintain precise stochiometry. Equilibrium is possible with comparative ease because the cadmium atoms can diffuse to the exposed surface through the solid at the elevated temperatures involved and thence be evaporated. In the vertical processes, on the other hand, only at one end is there an open surface at which equilibrium can be established, so that the diffusion path necessary for an atom to escape is very much longer and evaporation very much slower due to the consequently reduced concentration gradients.

In our experiments, where a small quantity of hydrogen is introduced to prevent sticking, it is to be expected that this will further amplify the above effect, since hydrogen can react with tellurium to form TeH_2 quite readily, and may therefore also tend to shift the atom ratio towards the cadmium rich side.

IV. FUTURE WORK

At this stage we can only reiterate the statements made in the previous quarterly report. Namely that development and optimization of the vertical zoning technique will predominate in the immediate future until reliable and reproducible operation is achieved. Once this goal has been established, further development will be directed toward optimizing those parameters which will affect the performance of the ultimate device.

Solar cell work, however, is currently being carried out on polished slices of the multi-crystalline CdTe, and this work will continue in the future. It consists of making np and pn junctions on the p-type and n-type material respectively, and testing these junctions for photovoltaic properties after attaching electrodes and leads. On the n-type material, noted in the report, thin silver layers are being electrochemically deposited or evaporated on to the surface. Following this, diffusion studies are to be carried out to determine some optimum parameters. It is hoped that in this way that the device preparation characteristics will be at least partly established when single crystal material becomes available.

REFERENCES

1. Lawson, W. P. and Nielsen, S. "Preparation of Single Crystals", Semiconductor Monograph. Butterworths Sci. Publ. London, 1958.